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54. Method of depositing a thin metallic film on a non-metallic substrate with intermediary deposition of hydrides by reactive cathode sputtering.

57. Method of depositing a high-adhesion thin metallic film on a non-metallic substrate through an intermediary deposition of hydrides. The metal hydrides, which are temporarily deposited by reactive cathode sputtering, are the target. This target consists of titanium or a titanium-based alloy and another metal such as vanadium, chrome, manganese, iron, cobalt, nickel, copper, zirconium, niobium, molybdenum, hafnium, tantalum, tungsten, rare earths and platinum. Main application: ceramics-metal brazing.

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The present invention involves a new method of depositing a thin metallic film on a non-metallic substrate.

It is well known that it is difficult to bond metals with other non-metallic materials, because metal does not adhere well to such materials: we say that metal does not "wet" well these materials, such as ceramics.

We will further mention the use of ceramics as a substrate; however, we have made this choice by convenience and have used it only as an illustration. This should not lead to a restrictive interpretation of the invention.

Due to differences of dilatation between metal and substrate, the metal-substrate connection is fragile, because it is not usually obtained at the temperature at which the unit will be used.

Therefore, it is always very difficult to obtain such connections.
In order to obtain a ceramics-metal connection by brazing, the following treatment is used: on ceramics, we apply a lacquer containing a fine powder of refractory metals, such as molybdenum and tungsten, as well as other components, which provide the bond between ceramics and metal, in suspension in a binder such as nitrocellulose. A film of this lacquer is applied on ceramics which is heat-treated at 1,600°C in a damp hydrogen atmosphere in order to obtain a thin metallic film on which brazing is performed. This heat treatment is a industrial binding operation. In addition, wetting can be improved by depositing an electrolytic nickel or copper coating of about ten microns before applying the braze which consists of silver-copper or gold-nickel alloys.

The French patent no. 949619 described a method of welding metals with metals and/or with glass or ceramics. This method consists of coating the connectioning parts with titanium hydride and vacuum heat or heat them in a neutral or reducing atmosphere.

The French patent no. 1228621 also described a method which relates to joining two refractory non-metallic objects or a refractory non-metallic object and a metallic component. This method consists of applying a thin film of metal hydride (titanium or zirconium hydride) on the joining surface of the non-metallic component and a welding film, then heating this surface in an inert atmosphere to break down the hydride and bond the metal to the welding.

However, the titanium hydride can not be used in industrial operations because of its low stability and reactivity - mainly with atmospheric water vapors.

In addition, the simple application of titanium hydride does not provide a resistant anchorage of metal on ceramics.

Moreover, we know the cathode sputtering technology: a method of depositing a material on a substrate in a chamber which contains a low-pressure inert gas.

An electrical field ionizes the gas which leads to the formation of a luminescent plasma. A burst on the "target material", which is fixed on an electrode with cathode potential, by mechanical effect, results in expulsion of atoms from the material surface, which will be deposited on the substrate in front of the target. When the depositing material is a metal, as in our example, this becomes a cathode.

It is possible to adapt the cathode shape to the substrate in order to obtain the appropriate deposition. For example, a tubular cathode allows a deposition on wires or pipes.

By superimposing a magnetic field over an electrical field in the proximity of the cathode (use a magnetron cathode), the electronic trajectories are more complex and the gas ionization increases, which provides a higher deposition rate.

It is possible to reduce the gas contamination of the sputtered film by ion bombardment using the sputtering with a substrate polarization method (a method usually called "bias sputtering").

Finally, the use of high-frequency alternating voltages has various advantages, mainly the possibility of using lower voltages than in the case of direct current.

In addition, it is known that the introduction of chemically active gas in the chamber generates "reactive sputtering": for example, the introduction of oxygen allows the deposition of oxides, the introduction of nitrogen or ammonia allows the deposition of nitrides, the introduction of hydrogen allows the deposition of hydrides, etc.

A mixture of reactive and inert gas is introduced. Usually, the inert gas is argon or krypton.

A general description of cathode sputtering methods, including examples, is provided in the "Thin Film Processes", by J.L. VOSSEN and W. KERN, Academic Press (1978).

We have discovered that it is possible to deposit highly adhesive thin titanium-based metallic film on a non-metallic substrate by reactive cathode sputtering.

The titanium hydride deposited by reactive cathode sputtering has many advantages for ceramic metallizing, particularly providing excellent adhesion, which allows brazing at high temperatures, higher or equal to 1,000°C.

However, the titanium has a disadvantage: a low sputtering rate. This disadvantage is worsened by the introduction of hydrogen during the reactive sputtering. The use of this method requires long sputtering time of about 30 minutes for a film with a minimum thickness of 0.5 microns. Therefore, it is important to increase the hydride deposition rate in order to obtain a better sputtering rate.

We have also discovered that, when a pure titanium film is not desired, it is possible to deposit highly adhesive thin titanium-based metallic film on a non-metallic substrate by reactive cathode sputtering of titane that has been mixed or alloyed with other metals which react with hydrogen.

The present invention relates to a method of depositing a highly adhesive thin metallic film on a non-metallic substrate through an intermediary deposition of hydrides. The metal hydrides, which are temporarily deposited by reactive cathode sputtering, are the target. This target consists of titanium or a titanium-based alloy and another metal such as vanadium, chrome, manganese, iron, cobalt, nickel, copper, zirconium, niobium, molybdenum, hafnium, tantalum, tungsten, rare earths and platinum.

In general, the target contains at least 50% titanium and one or several metals selected from the above-mentioned ones.

We would also like to mention lanthanum, ceryum, neodymium, etc. among the rare earths.

Some alloy metals can be mixed with titanium; for example, titanium can be mixed with the following alloys: LaNi5, MgNi or the mishcmetal consisting mainly of 52% ceryum, 25% lanthanum and 18% neodymium.

The targets are made by pressing and sintering the powder mix. The selection and composition of the target are based upon application.

After the deposition of the hydrate coating by cathode sputtering, this coating is transformed on metallic film by hydride decomposition - for example by heat, through heat treatment of the coated substrate or by brazing.

The method proposed through this invention provides highly adhesive metallic film with a specific target composition. A very pure titanium deposition can be obtained with a titanium target.

The decomposition of the hydride generates a close bond between substrate and metal and metallic depositions with excellent adhesion.

Thus, by exposing a ceramics tube, which was coated with titanium using the method of this invention, to high stress (high internal pressure and temperature of 800°C), a separation of the outside part of the tube is incurred. However, the ceramics will come out together with the metal. In other words, the separation is not the result of the destruction of the ceramics-metal bond but from the breaking of the bonds inside the ceramic. It is a surprising result taking into account the difficulties of bonding metal with ceramics using classic methods.

In addition, the method of the invention prevents the heat treatment at 1,600°C in a hydrogen atmosphere which is difficult to implement in an industrial environment.

The strength of the ceramics-metal bond is due mainly to the metallic hydrides which "wet" the substrate well, while a direct deposition of the same metal by cathode sputtering in a pure argon atmosphere does not wet the substrate well, and provides a deposition which is not sufficiently anchored to the substrate.

Among the substrates which are appropriate for metallic film depositions using the method of this invention are the ceramics - that is, solid materials with a polycristalline structure consisting of grains bonded together by compacting, followed by cooking or sintering. We particularly point out metallic oxide-based ceramics, for example magnesium, zirconium dioxide, alumina, beryllium oxide-based or alumina silicates, carbides, silicides or mixes of these compounds.

We can also use glass as a substrate, for example silica glass, vycor, etc.

In specific situations, the method described by this invention has the following characteristics, considered individually or in combination:

- The cathode sputtering is performed in an atmosphere that contains 4 to 20% hydrogen, the remainder being an inert gas; the inert gas can be argon or krypton; the percentage of hydrogen is usually 5-10% of the volume.
- The cathode sputtering is performed at pressures lower than 4.10^{-2} mm of mercury (approximately 5.3 Pa) - for example, at pressures ranging from 4.10^{-2} Hg to 10^{-3} mm Hg ($1.33.10^{-1}$ Pa).
- Use argon with at least 99.995% purity and hydrogen with at least 99.95% purity; we would like to point out that hydrogen isotopes are not considered impurities when evaluating hydrogen purity.
- Before the decomposition of the hydride, a film of the same metal or same metallic mixture, or other metals can be applied on the hydride coating, for example, by cathode sputtering in an inert atmosphere.
- The hydride is decomposed by heat treatment at a temperature of 400-600°C at high pressure, preferably under 10^{-5} mm mercury ($1.33.10^{-3}$ Pa), or a pressure ranging from 10^{-5} mm Hg to 10^{-7} mm Hg ($1.33.10^{-5}$ Pa).

The substrate, covered by a metallic hydride film through the method of this invention, can be vacuum-brazed directly on a support or other metallic part by means of classic brazing. This process consists of depositing the braze (for example, a brazing ring or wire) on the hydride coating, then applying the metallic part to the braze. The set is heat treated at low pressure - for example, lower than 10^{-5} mm Mercury up to the braze fusion temperature. At 400-600°C, the hydride decomposes and provides a close bond between the substrate and metal. At 900-1,000°C, the braze fuses and forms a braze-metal alloy. Then, the assembly is cooled down under normal conditions.

As indicated above, in the event that a simple deposition of metallic film on substrate is desired, it is possible to apply an additional metallic film of titanium or similar metallic mixture, or other metals, on the titanium hydride coating or titanium-based metallic mixture hydride coating, by cathode sputtering in an atmosphere of pure inert gas. Then, the set is vacuum heat treated at a temperature of 500–1,000°C to provide a substrate-metal bond and possibly the diffusion of the metal of the second coating into the first one. At this point, an additional metallic film can be electrolytically deposited to thicken the metallic film.

In a version of the method described in this invention, the target is cooled only partially so that the substrate can be heated by radiation at a temperature of approximately 400°C. Under these conditions, the deposited hydride decomposes when coming in contact with the substrate during the cathode sputtering process, providing the metal substrate bond without any other heat treatment.

One of the advantages of this method is that the target which contains nickel can be heated to a temperature higher than the Curie temperature of the nickel. This allows the use of the magnetron effect which is impossible to obtain at ambient temperature due to the magnetic properties of the nickel.

The following examples illustrate the invention without limiting it:

<u>EXAMPLE 1</u> – deposition of a titanium hydride film on brazing ceramics

The substrate is a pure alumina square plate with a side of 2.5 cm and a thickness of 0.5 mm.

The titanium hydride is deposited by reactive cathode sputtering.

The experimental conditions are the following:

- ALCATEL SCM 441 sputtering station
- composition of gas mixture: 90% argon U – 10% hydrogen U
- Pressure: 6.10^{-3} mbar (0.6 Pa)
- Titanium magnetron target with a diameter of 10 cm
- Power: 500 watts corresponding to a voltage of 800 volts on the target.
- Radiofrequency sputtering with a voltage of 60 volts on the substrate support.
- Target-substrate distance: 4 cm
- Sputtering time: 30 minutes for a thickness of 1 micrometer of titanium hydride.

Argon U is sold by "Air Liquide" Company.

It contains the following impurities: $N_2 < 40$ ppm

$O_2 < 5$ ppm

$H_2O < 5$ ppm

Hydrogen U (sold by "air Liquide" Company) has the following characteristics: purity 99.95%, the remaining 5% consisting mainly of impurities, such as: nitrogen, oxygen, water.

The deposition of titanium hydride is shiny, slightly golden (while titanium is gray). The presence of the hydrogen in the deposited film (hydride) can be detected by nuclear magnetic resonance or by x-rays when the deposition is crystallised.

The coated ceramics can be directly vacuum-brazed on its support.

To this purpose, apply a ring with an outside diameter of 16 mm of EL 36 brazing wire (Comptoir Lyon Alemand Louyot-Paris). This is an alloy made of 82% gold and 18% nickel which melts at 950°C.

On the braze ring with a thickness of 0.5 mm, apply a cylinder of Dilver P alloy with an outside diameter of 16 mm, thickness of 0.5 mm and height of 5 mm.

The set is subjected to heat treatment of increasing temperature for 3 hours until it reaches 1,000°C at a low pressure of 10^{-5} mm Mercury ($1.33.10^{-3}$ Pa).

After several minutes of heat treatment at this temperature, the set is cooled down slowly.

The obtained braze is separation resistant and can withstand temperature of up to 800°C.

EXAMPLE 2 – Deposition of titanium film on alumina tube:
Follow the same steps as in the previous example to deposit a titanium hydride film (thickness: approx. 1 micrometer) on the outside of an alumina tube.

Apply a nickel film of several microns by cathode sputtering under identical conditions in a pure argon atmosphere. Then, add an electrolytic nickel film with a thickness of 5 micrometers.

The outside nickel film is intended to protect the titanium from oxidation.

The set is vacuum heat-treated between 500 and 1,000°C to decompose the hydride and provide the titanium-ceramics bond and the nickel diffusion in titanium.

A metal-ceramics bond is obtained which, as it has already been mentioned, has a higher adhesion than the ceramics. At a heat treatment of 800°C and an internal pressure of 20 bars (2.106 Pa), the outside ceramics coating is separated - not the metal alone.

EXAMPLE 3 – Deposition of a titanium and iron hydride coating on ceramics.

The substrate is an off-the shelf pure alumina square plate with a side of 2.5 cm and a thickness of 0.6 mm.
The titanium hydride is deposited by reactive cathode sputtering with a sintered target containing (% in weight) Ti 70% - Fe 30%.

The experimental conditions are the following:

- ALCATEL SCM 441 sputtering station for magnetron of cathode sputtering.
- Gas mixture composition: 80% argon U, 20% hydrogen U.
- Pressure: 5.10^{-3} mbar (0.5 Pa)
- Power: 500 watts at a voltage of 800 volts on the target.
- Target-substrate distance: 4 cm.
- Sputtering time: 30 minutes.

The deposition rate is 5.2 Angstroms per second, while under the same conditions, it is only 4 Angstroms per second for pure titanium.

The presence of the hydrogen in the deposited coating (hydride) can be demonstrated by nuclear magnetic resonance or by x-ray analysis if the deposition is crystallised.

The coated ceramics can be directly vacuum brazed on its support or, preferably, after depositing a copper or nickel coating - for example, by cathode sputtering.

To this purpose, apply a ring with an outside diameter of 16 mm of EL 36 brazing wire (Comptoir Lyon Alemand Louyot-Paris). This is an alloy made of 82% gold and 18% nickel which melts at 950°C.

On the braze ring with a thickness of 0.5 mm, apply a cylinder of Dilver P alloy with an outside diameter of 16 mm, thickness of 0.5 mm and height of 5 mm.

The set is subjected to heat treatment at increasing temperature for approximately 3 hours until it reaches 1,000°C at a low pressure of 10^{-5} mm Mercury ($1.33.10^{-3}$ Pa).

After several minutes of heat treatment of this temperature, the set is cooled down slowly.

The obtained braze is tear resistant and can withstand temperature of up to 800°C.

EXAMPLE 4 – Deposition of a titanium and manganese coating on alumina plate.

Follow the same steps as for the deposition of a hydride coating using a sintered target with the following target: 60% Ti – 40% Mn. The deposition rate is 5.7 Angstroms/second.

Then, apply a copper coating of several microns by cathode sputtering under identical conditions in a pure argon atmosphere.

The set is vacuum heat-treated between 500 and 1,000°C to decompose the hydride and provide the metal-ceramics bond.

Follow the same steps for the deposition of metallic film by reactive cathode sputtering with intermediary deposition of corresponding metallic hydrides using targets with the following compositions:

EXAMPLE 5
90% Ti – 10% $LaNi_5$
Deposition rate: 6 Angstroms/second

EXAMPLE 6
Target composition: 50% Ti – 50% Cr
Deposition rate: 6 Angstroms/second

EXAMPLE 7
Target composition: 95% Ti – 5% Mg_2Ni
Deposition rate: 8 Angstroms/second

PATENT CLAIMS

1. Method of depositing a high-adhesion thin metallic film on a non-metallic substrate through an intermediary deposition of hydrides. The metal hydrides, which are temporarily deposited by reactive cathode sputtering, are the target. This target consists of titanium or a titanium-based alloy and another metal such as, vanadium, chrome, manganese, iron, cobalt, nickel, copper, zirconium, niobium, molybdenum, hafnium, tantalum, tungsten, rare earths and platinum.
2. Method, in accordance with claim 1, in which the target contains at least 50% titanium in weight.
3. Method, in accordance with any of the previous claims, in which the substrate is ceramics or glass.
4. Method, in accordance with claim 3, in which the ceramics are selected among those metallic oxide-based - for example, magnesium, zirconium, alumina, berylium oxide-based or alumina silicates, carbides, silicides or mixtures of these compounds.
5. Method, in accordance with any of the previous claims, in which the cathode sputtering is performed in an atmosphere that contains a volume of 20% hydrogen, the remainder consisting of inert gas.
6. Method, in accordance with claim 5, in which the volume of hydrogen is 5 – 10%.
7. Method, in accordance with any of the previous claims, in which the cathode sputtering is performed at pressures lower than 4.10-2 mm Mercury (approximately 5.3 Pa).
8. Method, in accordance with claim 7, in which the cathode sputtering is performed at pressures ranging from 4.10-2 mm Mercury to 10-3 mm Mercury (1.33.10-1 Pa).
9. Method, in accordance with any of the previous claims, in which a coating of titanium or the same titanium-based metallic mixture or other metals is deposited on the hydride coating before the hydride decomposition.
10. Method, in accordance with any of the previous claims, in which the hydride is decomposed by heat treatment at low pressure.

11. Method, in accordance with claim 10, in which the heat treatment is performed at a temperature of 400-600 C at a pressure lower than 10-5 mm Mercury (1.33.10-3 Pa).
12. Method, in accordance with any of the claims 1 – 8, in which the braze is deposited on the hydride coating; then a metallic part is applied on the braze which fixes to the substrate. The set is subjected to heat treatment which results in hydride decomposition and providing a close bond between the substrate and the deposited metal, as well as providing the fusion of the brazing under normal conditions.
13. Method, in accordance with any of the claims 1 – 8, in which the depositing metal target is partially cooled in order to heat the substrate by radiation at a temperature of at least 400 C, and under these conditions the hydride decomposition is performed directly on contact with the substrate during the cathode sputtering without any other heat treatment.

CERTIFICATION OF TRANSLATION

BEFORE ME PERSONALLY APPEARS ***Jessica Diaz***, Language Coordinator at Languages Unlimited, **WHO DEPOSES AND SAYS THAT** ***Miheala Meci*** **HAS PERFORMED THIS TRANSLATION FROM** ***French*** **TO** ***English***, **AND SHE IS FULLY VERSED IN THESE LANGUAGES AND HAS DONE THIS TRANSLATION OF** ***Patent*** TO THE BEST OF HER ABILITY. THE SOURCE DOCUMENT CONSISTING OF 12 PAGE(S), AND THE TRANSLATION CONSISTING OF 12 PAGE(S); THIS **CERTIFICATION BEING ATTACHED THERETO.**

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